ABB Lummus Global, Inc. (formerly ABB Lummus Crest)

A Safe, Environmentally Friendly Method to Produce Alkylate

High-octane alkylate is used as a gasoline blend stock to raise octane and reduce automobile emissions. In 1995, refiners typically used liquid acid catalysts (hydrofluoric acid or sulfuric acid) to promote and enhance the speed of the chemical reactions to produce alkylate. However, liquid acids pose serious safety and handling problems, including potential life-threatening accidents. ABB Lummus Crest (the name was changed to ABB Lummus Global Inc. in 1995) submitted a proposal to the Advanced Technology Program (ATP) to develop a solid acid catalyst, which would be a safer, more economical substitute catalyst for the alkylate process. ABB would develop a thin-film catalyst layer to be deposited on a small pellet-like carrier. Previous attempts to develop solid acid catalysts had failed due to pore blockage and short catalyst life. Numerous technical risks included identifying an acceptable inert support structure for the thin-film catalyst, activating the catalyst, and developing a means to regenerate the catalyst at the refiner's site. If successful, ABB believed the solid acid catalyst process could retrofit existing U.S. alkylate plants. If retrofitted in all 112 domestic plants, the process could save approximately $580 million in processing costs per year.

ATP awarded cost-shared funding for a three-year project as part of a focused program, "Catalysis and Biocatalysis Technologies," in 1995. By the end of the project, ABB was able to deposit a thin layer of active catalyst on a small, inert, pellet-shaped support and regenerate the catalyst quickly. They were granted a patent covering the method of preparation for this catalyst. Furthermore, the company developed a reactor design to perform the process efficiently for which they applied for patent coverage. Based on their achievements, ABB continued development and formed a joint venture in 2001 with Akzo Nobel (a catalyst manufacturer whose name was changed in 2004 to Albemarle Corp. through an acquisition) and Fortum Oil and Gas, an energy company (whose name was changed to Neste Oil Corporation in 2005, as a result of a restructuring). The joint venture partners developed and optimized a solid acid alkylation demonstration plant that produced 10 barrels per day from 2002 to 2004. As of 2005, the joint venture was in negotiations with several large energy companies to establish the first commercial-scale plant to produce upwards of 10,000 barrels per day. Analysts predict that growing global demand for alkylate will require 40 to 50 new plants by 2015.

COMPOSITE PERFORMANCE SCORE
(based on a four star rating)
* * *

Research and data for Status Report 95-05-0034 were collected during December 2004 – February 2005.

Liquid Acid Catalysts Pose Significant Risks

Gasoline is manufactured by combining several petroleum-based components to meet octane, oxygenate, and environmental standards. Alkylate is an ideal component, because it makes fuels more environmentally sound and is very high in octane (higher than 90). Demand for fuel containing increasing amounts of alkylate has grown as the number of fuel-environmental standards has increased.

Developed during World War II to produce high-octane gasoline for aircraft, conventional methods to process alkylate rely on liquid acid catalysts, either hydrofluoric or sulfuric acids. (Catalysts increase the speed and efficiency of the chemical reactions.) Later, alkylate's main application evolved as a component in unleaded and premium grades of automobile gasoline. However, both hydrofluoric acid and sulfuric acid are very corrosive and can cause serious injury through skin contact or inhalation. A few well-publicized accidents in the United States involving hydrofluoric acid in the late 1980s resulted in significant leakage, exposure, and injury. Thus, production methods that use liquid acid pose a potential threat to plant workers and to the surrounding communities. Extensive safety precautions and complex permit processes can make liquid acid methods expensive. In addition, liquid acid processing results in an unwanted heavy hydrocarbon (oil) byproduct called acid-soluble oil, which can be difficult to recover and dispose.

Two types of solid catalysts had already been studied unsuccessfully. One type consisted of active materials adsorbed on inert supports of alumina or silica. One difficulty with this type of solid catalyst was the high cost of the active components. Furthermore, the catalyst reacted slowly with the support in the presence of moisture and then lost activity. Disposing of the spent catalyst posed environmental problems. The second type of solid catalyst contained acidic (heteropoly acids) or "superacid" supports. The active catalyst constituents did not leach out, and they could be regenerated conveniently. The main problem with these solid catalysts, however, was that their initial high activity decreased rapidly, because heavy alkylation byproducts blocked the pores of the catalyst support.

ABB Lummus Proposes to Develop Solid Acid Catalysts

ABB Lummus Crest (ABB) was an engineering and construction company with customers in the oil and gas refining industry. ABB proposed to develop a new, environmentally superior process to make alkylate. Company researchers had to address the following technical risks:

- Identify acceptable inert support structure for the thin layer of alumina catalyst
- Identify an appropriate activation procedure to form the active catalyst
- Produce a catalyst with sufficient concentration of active sites per unit of reactor volume
- Maintain catalyst activity for a target 1,000 kg alkylate per 1 kg of catalyst
- Regenerate the catalyst on site at the refinery
- Improve the catalyst's safety and environmental characteristics (compared with hydrofluoric and sulfuric acid)
- Integrate the catalyst with the refineries' reactors, in order to retrofit existing plants that currently rely on hydrofluoric and sulfuric acid

Because of these risks, ABB was unable to fund the research internally. ATP awarded cost-shared funding for a three-year project beginning in 1995 as part of a focused program, "Catalysis and Biocatalysis Technologies." If successful, ABB believed solid acid alkylation could save U.S. refiners an estimated $580 million in processing costs per year based on retrofitting 112 domestic alkylation facilities. Another potential benefit of solid acid catalysis would be reducing or eliminating the unwanted heavy oils that result from liquid acid processes. The primary benefit would be increased safety for communities and plant workers, because solid acid processing does not have the health and safety risks that are associated with transporting and utilizing liquid acids.

ABB Completes Laboratory-Scale Reactor

In 1995, soon after the start of the project, ABB Lummus Crest merged with ABB Global Engineering to form ABB Lummus Global Inc. During the first year of the project, ABB intended to develop the catalyst supports, the methods of forming the thin layer of oxide film on the supports, and the procedure for activating the catalyst. During the second and third years, ABB would develop the proposed solid acid catalyst and would focus on laboratory catalyst testing, regeneration studies, reactor engineering studies, catalyst manufacturing, process engineering, and process economics to guide research. Contact with potential clients would provide feedback to make adjustments to the process during development. ABB began to explore solid acid catalysis with the following partners: Glatt Air

Techniques, Inc., the Department of Ceramics Engineering at Rutgers University, Niro Inc., Norton Chemical Process Products Corp. (later renamed Saint-Gobain NorPro Corp.), and Vector Corp. ABB also relied on consultants at Applied Research and Technology and formed a key cooperative relationship with Akzo Nobel, a catalyst manufacturer, in 1996.

ABB's research covered five primary areas:

- **Thin-film formation and catalyst activation**. ABB developed the methodology to form thin-film oxide or other catalyst precursors on a suitable support. Vector Corp. provided thin-film coating processes. Niro, Inc. conducted alternative film formation tests, but these did not produce satisfactory thin-film coatings. Glatt Air Techniques, Inc. conducted more successful film formation tests in a Wurster Fluid Bed Coater. Norton Chemical Process Products Corp. supplied the inert alpha alumina pellets onto which the coatings are applied. ABB prepared the active chlorinated alumina thin-film catalyst that had the desired acidity and stability and applied it to the support.

- **Surface features' effects on catalyst performance**. ABB measured the relationship between surface features of thin-film catalysts in order to improve their performance for alkylation. A good catalyst has high activity and selectivity. Activity refers to the capacity of a chemical to take part in a chemical reaction; selectivity refers to the catalyst's ability to promote a desired reaction rather than undesired reactions that reduce the yield of the desired product. ABB was able to demonstrate that solid acid alkylation resulted in higher selectivity than sulfuric acid alkylation. Activity remained stable.

- **Solid acid catalyst testing**. ABB tested five catalysts: beta zeolite, paraffin isomerization type catalyst, a proprietary catalyst from Hydrocarbon Technologies Inc., another alumina catalyst, and a proprietary catalyst developed by Akzo Nobel. Because the Akzo Nobel catalyst showed the most promise, ABB prepared and tested a thin film adaptation of it.

- **Catalyst regeneration**. A significant problem for solid acid alkylation was that these catalysts fouled quickly, lost activity, and required frequent regeneration. ABB needed to find a way to clean the catalyst and bring it back to fresh activity. The company demonstrated low-temperature regeneration with hydrogen, performing five cycles of alkylation and regeneration. Results during the project indicated good recovery of catalyst activity after each regeneration, with good stability.

- **Reactor engineering**. ABB developed a kinetic model and investigated several commercial reactor concepts. They built and tested a series of reactors with varied flows of reaction products and filed a patent application for their optimized reactor system. They designed and built a laboratory-scale reactor to simulate one stage of a commercial reactor.

In 1997, ABB and Akzo Nobel initiated a cooperative program to evaluate the alumina thin-film catalyst and an alternative, proprietary Akzo-developed catalyst. Their intent was to move forward jointly in developing, piloting, and commercializing the final preferred alkylation process.

Catalyst production methods that use liquid acid pose a potential threat to plant workers and to the surrounding communities

For the remainder of the ATP-funded project, ABB and Akzo conducted further testing of three catalysts: chlorinated thin-film alumina catalyst (the main focus of this project), a proprietary catalyst developed by Akzo Nobel, and a thin-film adaptation of the Akzo Nobel catalyst. They developed a reactor concept for a commercial solid acid alkylation plant for each of the three alternatives. The companies optimized feed materials and process parameters for alkylation. They developed and demonstrated regeneration cycles on a laboratory scale and finally selected the catalyst that had the best regeneration characteristics. ABB received a patent for their technology advances and published their results in academic journals. Key accomplishments from the ATP-funded research included the production of efficient, solid acid catalysts on inert substrates; demonstration of the catalyst regeneration process; and the reactor design concepts. These advances could not have been accomplished without ATP support.

Researchers Seek a Third Joint Venture Partner

After ATP funding ended in 1998, ABB and Akzo continued developing their solid acid alkylation process. Prior to commercialization, ABB and Akzo needed to resolve size and capacity scale-up issues and develop business plans for manufacturing with solid acids. Their goal was to achieve at least economic parity with hydrofluoric and sulfuric acid process methods. They developed a concept for a demonstration plant, which included technical designs, capacity goals, and general layout. The goal was to determine whether large-plant manufacturing was feasible after achieving success in the demonstration plant and determining the likelihood of technical and economic success in a commercial plant. At this point, another partner was needed, so that ABB and Akzo could develop a prototype plant located at or near an existing refiner.

ABB believed solid acid alkylation could save U.S. refiners an estimated $580 million in processing costs per year.

Fortum Oil and Gas joined the joint venture in 2001. Fortum was an energy company with an ongoing interest in developing solid acid catalysts. The company had participated in similar prototype plant development efforts about 10 years earlier. Together, the three companies developed a prototype plant located in Porvoo, Finland (see illustration) that began operation in 2002. The plant used the reactor design concepts and catalyst regeneration methods developed during the ATP-funded research. The prototype plant provided the complete cycle of alkylation, including catalyst regeneration, at a fully scalable capacity. If successful, the concepts would be scaled up to a commercial-scale process, which produces upwards of 10,000 barrels of alkylate per day (one barrel equals 42 U.S. gallons). Furthermore, handling and safety concerns were dramatically reduced at the prototype plant, as the safe-to-handle solid acid catalyst pellets were utilized in place of the conventional toxic and corrosive liquid acids. The pellets could be delivered in plastic bags or metal drums.


The photo on the left shows an outside view of the solid acid alkylation pilot plant built and operated by the joint venture partners from 2002 to 2004 in Porvoo, Finland. The plant was used to optimize and demonstrate the process. An internal view of the reactors is shown on the right.

The demonstration plant proved that the solid acid catalyst yields high-quality alkylate, with maximized activity and stability. The process was robust, with low sensitivity towards feedstock variation and common impurities. One key to the process success is cyclic reactor operation; that is, alternating periods of alkylation and mild catalyst regeneration, which allows the plant to operate continuously and maintain product quality.

Joint Venture Set to Commercialize “AlkyClean”

In October 2004, ABB, Akzo Nobel, and Fortum Oil and Gas completed their demonstration project. (The Akzo Nobel refinery catalyst business was purchased by a U.S. firm, Albemarle Corp., in 2004. Fortum was renamed Neste Oil Corporation in 2005.) The joint venture partners announced publicly that they had developed a new, environmentally superior process to make alkylate, which achieved a similar alkylate product at a cost that was comparable to the liquid acid catalyst process. Moreover, the process used is safer, because the solid acid catalyst pellets for this “green technology” are neither toxic nor corrosive, unlike liquid acids, which must be transported to the refinery and utilized under strict safety precautions. Furthermore, the solid acid process “…generates gasoline of the highest quality. Moreover, this robust process is reliable, no unnecessary byproducts are produced, and plant investment is considerably lower than with the old technology,” said Philip Angevine, manager of the Ultra-Clean Fuels program at ABB. ABB, Albemarle, and Neste expect that their solid acid alkylation process, called “AlkyClean,” will fill a crucial refining niche.

Because AlkyClean processing is economically competitive with liquid acids, without the environmental safety concerns, ABB Lummus and its joint venture partners anticipate that oil refinery firms will choose their technology for new alkylation plants. ABB will license the new technology for both new plants and retrofitting existing plants. The technology will be typically transferred via an engineering design package, with drawings and all the specifications and instructions to build and operate the plant. ABB representatives will support the plant as technical consultants throughout the life cycle of the unit.

Alkylation Demand Is Expected to Rise

As of 2004, the U.S. catalyst market was growing at 4.5 percent per year, boosted by demand for catalysts that help to reduce pollution. The increase in global demand for alkylate by 2015 will reach an estimated 400,000 to 500,000 barrels per day (or the equivalent of 40 to 50 new alkylation plants). The AlkyClean process is economically competitive with existing hydrofluoric and sulfuric acid processes. Analysts predict that alkylate will gain market share as refineries update their processes to meet more stringent environmental regulations for fuels anticipated by 2010 to 2015. Furthermore, its commercial potential will grow as existing plants age. For example, energy companies are likely to find it more difficult to renew permits at existing hydrofluoric acid and sulfuric acid alkylation plants because of environmental, safety and homeland security concerns. These concerns could necessitate new plant construction or retrofitting where applicable.

Conclusion

ABB Lummus Crest (renamed ABB Lummus Global in 1995) successfully developed solid acid alkylation catalyst technology as an alternative to existing liquid acid processes that rely on corrosive and toxic hydrofluoric and sulfuric acids. ABB received one patent for this technology and published its findings in academic journals. ABB formed a joint venture with Akzo Nobel (a catalyst manufacturer, later acquired by Albemarle Corp.) and Fortum Oil and Gas (an energy company, renamed Neste Oil under a restructuring in 2005) to operate a successful demonstration plant from 2002 to 2004. At the prototype plant, they produced alkylate at a reliably scalable fraction of a commercial plant that generally produces about 10,000 barrels per day. As of 2005, the joint venture was seeking agreements to establish the first commercial plants. Analysts predict that the alkylate market demand will grow by the equivalent of 40 to 50 new plants by 2015, due to rising environmental standards and increasing demand for fuel. Many of the existing 170 plants worldwide (most are in the United States) will need to be replaced or retrofitted within that time, as well, so the commercial potential for this technology remains strong.

PROJECT HIGHLIGHTS
ABB Lummus Global, Inc. (formerly ABB Lummus Crest)

Project Title: A Safe, Environmentally Friendly Method to Produce Alkylate (Thin-Film Solid Acid Catalyst for Refinery Alkylation)

Project: To develop a long-life, solid acid catalyst for use in the economical, environmentally friendly production of high-octane refinery alkylate.

Duration: 9/1/1995–8/31/1998
ATP Number: 95-05-0034

Funding(in thousands):**

ATP Final Cost	$1,504	46%
Participant Final Cost	1,800	54%
Total	$3,304	

Accomplishments: ABB Lummus Global, Inc. (formerly ABB Lummus Crest) achieved 100 percent of its technical goals:

- **Thin-film formation and catalyst activation**. ABB formed thin-film oxide or other catalyst precursors on inert support pellets and achieved desired acidity and stability.
- **Catalyst performance**. ABB demonstrated that solid acid alkylation resulted in higher selectivity than sulfuric acid alkylation. Selectivity means that the catalyst promotes desired reactions rather than undesired reactions, so that the highest purity product is achieved.
- **Testing solid acid catalysts**. ABB tested five catalysts and selected a proprietary catalyst developed by Akzo Nobel, which was the most efficient.
- **Catalyst regeneration**. Solid acid catalysts fouled quickly and were deactivated. A key milestone for this project was developing a means to regenerate catalysts (cleaning them and bringing them back to activity). ABB demonstrated good recovery of catalyst activity after each regeneration, with good stability.
- **Reactor engineering**. ABB developed models and commercial reactor concepts for its various catalyst samples. After selecting the best catalyst, they optimized the reactor system. They built a laboratory-scale reactor to simulate a commercial reactor.

After ATP funding ended, ABB continued its collaboration with Akzo Nobel, a catalyst manufacturer. Together, they formed a joint venture with Fortum Oil and Gas, an energy company, in 2001 to demonstrate and optimize the solid acid catalyst based alkylation process technology at a demonstration-scale plant located near an existing refinery. The demonstration plant operated from 2002 to 2004 (Fortum was renamed Neste Oil Corp. in 2005) with the following results:

- The joint venture developed "AlkyClean catalyst," which are solid acid catalyst pellets that are delivered to the refinery in plastic bags or metal drums. Use of the pellets eliminates the transporting, processing and handling risks associated with toxic and corrosive liquid acids.
- The solid-acid-catalyst-based AlkyClean process yielded high-quality alkylate, at a cost that is economically comparable to liquid acid processes.
- The solid acid catalyst process showed low sensitivity towards feedstock variation and impurities.
- Alternating cycles of alkylation and catalyst regeneration allowed the plant to operate continuously and maintain product quality.

ABB filed three patent applications from this ATP-funded technology, with the following one patent awarded:

- "Catalyst and method of preparation"
  (No. 5,935,889: filed October 4, 1996; granted August 10, 1999)

Commercialization Status: ABB has now proven and optimized solid acid alkylation at its demonstration-scale plant. Together with joint venture partners Albemarle Corp. and Neste Oil Corp., ABB is negotiating with energy companies to establish the first commercial plants, which will produce upwards of 10,000 barrels per day.

** As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs.
Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.

PROJECT HIGHLIGHTS
ABB Lummus Global, Inc. (formerly ABB Lummus Crest)

Outlook: The outlook for solid acid catalyst alkylation is strong. Alkylate can meet the rising demand for high-octane and low-emission gasoline. Solid acid alkylation is a safer, cost-effective alternative to existing hydrofluoric acid and sulfuric acid processes. Construction of 40 to 50 new alkylation plants is anticipated by 2015. In addition, as the existing 112 U.S. alkylation plants age, environmental safety and homeland security concerns will increase the likelihood of refiners choosing ABB's AlkyClean technology.

Composite Performance Score: * * *

Focused Program: Catalysis and Biocatalysis Technologies, 1995

Company:

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Subcontractors:

- Glatt Air Techniques, Inc.
  Ramsey, NJ
- Department of Ceramics Engineering
  Rutgers University
  Piscataway, NJ
- Niro, Inc.
  Columbia, MD
- Saint-Gobain NorPro Corp. (formerly Norton Chemical Process Products Corp.)
  Akron, OH
- Vector Corp.
  Cranbury, NJ

Publications: ABB researchers disseminated their findings through the publications listed below.

- Ercan, C., F. M. Dautzenberg, C. Y. Yeh, and H. E. Barner. "Mass-Transfer Effects in Liquid-Phase Alkylation of Benzene with Zeolite Catalysts," *Industrial and Engineering Chemistry Research*, v. 37, no. 5, 1724-1728, May 1998.
- D'Amico, V. J. "New Solid Acid Alkylation Process for Motor Gasoline Production," *ABB Review*, 71-76, February 2000.
- Raseev, S. D., D. G. Suciu, and S. Raseev. *Thermal and Catalytic Processes in Petroleum Refining*. New York: Marcel Dekker, 2003.
- Dautzenberg, F. M. and P. J. Angevine. "Encouraging Innovation in Catalysis," *Catalysis Today*, August 2004.

Presentations: ABB researchers also shared their findings through the presentations listed below.

- Dautzenberg, F. M., H. E. Barner, and Maraschino, M. "Integration of Catalysis and Reaction Engineering for New Refinery Technology," CATCON'98, Houston, TX, June 1998.
- Barner, H. E., C. Ercan, A. Khonsari, J. T. Kwon, L. L. Murrell, A. Westner, and F. M. Dautzenberg. "Thin Film Solid Acid Catalyst for Refinery Alkylation," ATP Fall Meeting, Atlanta, GA, November 1998.
- Broekhoven, E. I., V. J. D'Amico, P. J. Nat, H. Nousiainen, and J. Jakkula. "The AlkyClean Process: A New Solid Acid Catalyst Gasoline Alkylation Technology," National Petrochemical and Refiners Association Annual Meeting, San Antonio, TX, March 2002.
- Dautzenberg, F. M. "Hydro- and Dehydrogenation of Large Volume Petrochemicals," Roermond Conference on Catalysis, Rolduc-Kerkrade, The Netherlands, June-July 2002.
- Dautzenberg, F. M. "Intra-reactor Process intensification," Symposium for Emerging Technologies, Antwerp, Belgium, May 2003.
- D'Amico, V. J., E. H. Broekhoven, and H. U. Nousiainen. "AlkyClean Solid Acid Alkylation: Will It Finally Become a Reality?" Akzo Nobel Catalysts SCOPE Symposium, Florence, Italy, June 2004.